

6. CONCRETE SERVICE LIFE REGARDING CHLORIDE PENETRATION

6.1 Physicochemical considerations

6.1.1 *The significance of the problem*

Numerous surveys have indicated that chloride ions (Cl^-), originating from de-icing salts or seawater, are the primary cause of reinforcing steel corrosion in highways and marine or coastal structures [1,4,7-10]. The chlorides that transported through the concrete pore network and microcracks depassivate the oxide film covering the reinforcing steel and accelerate the reaction of corrosion and concrete deterioration, see Fig. 6.1.1. Even high-performance concrete may not necessarily ensure long-term durability in a severe environment unless it is designed for dimensional stability and soundness [5].



Figure 6.1.1 Photo of deteriorated concrete element due to reinforcement corrosion induced by chloride attack.

Chloride penetration is a process which takes place in totally or partly water-filled pores. This is the main reason that as a process is much slower than carbonation, where CO₂ molecule may penetrate faster via air-filled pores.

6.1.2 Sources of chlorides in concrete

Concrete is a porous material. Its solid skeleton consists of gravel and sand, bound together by the hardened cement paste. Its pores are partly or completely filled with water. The degree of pore saturation depends on their size and on relative humidity of the environment.

The source of chlorides in concrete may be *internal or external*. In the former and less common case, chlorides are present in the concrete from the very beginning. This is the case if chloride-containing admixtures are used in the concrete mix (e.g. CaCl₂ is a main constituent of many admixtures added to accelerate the setting and hardening of concrete), or if seawater or beach aggregates are used in the concrete construction in coastal or marine regions away from supplies of nonsaline materials.

In most cases of reinforcement corrosion due to chlorides, the source of chlorides is external. The use of de-icing salts in roads and highways during the winter is widespread in cold climates. Chlorides in these salts, dissolved in water, find easily their way into the concrete of bridge decks and abutments, into that of parking garages, etc. In marine environments, concrete is in contact with sea-water, continuously in the submerged parts or periodically in the tidal and splash zone. In coastal areas, air and mist blown inland from the sea are laden with salts. Chlorides that reach the concrete surface in this or the other way, enter the pore system either by diffusion in stationary pore water or by capillary suction of the surface water in which they are dissolved, or by combination of both transport mechanisms.

6.1.3 Main physicochemical processes

Almost in the majority of papers, chloride transport in concrete is modelled using the *Fick's second law of diffusion neglecting the chloride interaction with the solid phase*. However, it is

widely proved that chlorides are bound from concrete components in a percentage 30-60% depending on cementitious materials' composition and content [31,81]. Several field studies in recent years have indicated that the use of this law is not applicable to long-term chloride transport in concrete, calculating very often a decreasing chloride transport coefficient in time [94]. It is widely accepted that the transport behaviour of chloride ions in concrete is a more complex and complicated process than can be described by Fick's law of diffusion [95-97]. This approach, therefore, can be characterized as semi-empirical, resulting in the calculation of an "apparent" effective diffusivity. Thus, a term of adsorption-reaction of chlorides in concrete has definitely to be considered in an accurate model, see Fig. 6.1.2. Otherwise, using only the term of diffusion, despite satisfactory approach of the experimental results, the yielded "diffusivity" coefficient is not valid for other applications and predictions.

There is a generally good correlation between C_3A -content (or C_4AF when there is lack of C_3A -phase) and chloride binding capacity. There is also evidence for the binding of chlorides in CSH gel, possibly in interlayer space [98]. The Na^+ ions can be bound in CSH gel lattice [99], especially when the C/S ratio is low [20]. Several secondary chloride-calcium compounds have also been reported [100].

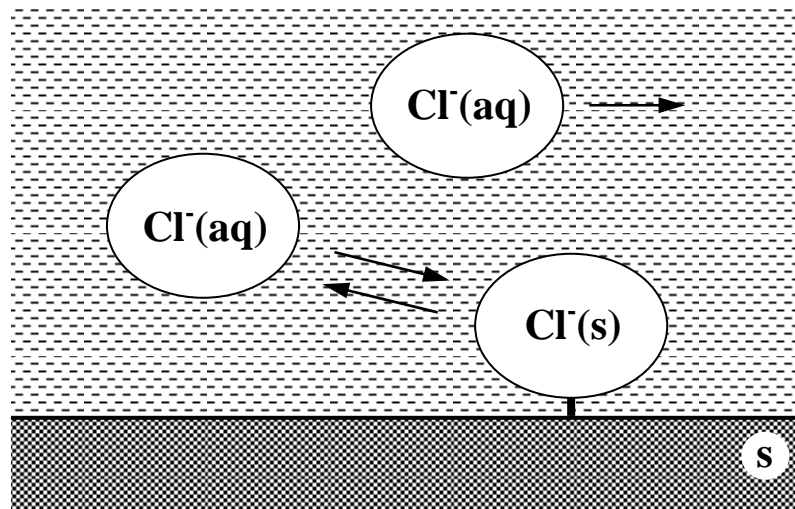


Figure 6.1.2 Schematic representation of chloride ion diffusion in water-saturated pores of concrete and its partial binding from the solid phase of concrete.

In addition to the chemical binding, the effects of ionic interaction, lagging motion of cations and formation of an electrical double layer on the solid surface all play an important role in the transport of chloride ions in concrete [96]. The relationship between bound and free chlorides is non-linear and may be expressed by the Langmuir equation [101], the Freundlich equation or the modified BET equation [97]. Of these, the Langmuir equation is both fundamental and easier to use in practical applications.

6.2 Theoretical model

6.2.1 Mass balances

Pereira and Hegedus [101] were the first to identify and model *chloride diffusion and reaction* in fully saturated concrete as a *Langmuirian equilibrium process coupled with Fickian diffusion*. Furthermore, Papadakis et al. [102,103] generalized this pioneering effort, offering an alternative simpler, yet equally accurate, numerical and analytical solution. By introducing a chloride-solid phase interaction term in the equations the calculation of an “*intrinsic*” *effective diffusivity* is possible. The *physicochemical processes* of diffusion of Cl^- in the aqueous phase of pores, their adsorption and binding in the solid phase of concrete, and their desorption therefrom are described by a nonlinear partial differential equation for the concentration of Cl^- in the aqueous phase $[\text{Cl}^-(\text{aq})]$ (in kg/m^3 pore solution), from which that of Cl^- bound in the solid phase $[\text{Cl}^-(\text{s})]$ (kg/m^3 concrete) can be computed algebraically:

$$\frac{\partial [\text{Cl}^-(\text{aq})]}{\partial t} = \frac{D_{e,\text{Cl}^-} (1 + K_{eq} [\text{Cl}^-(\text{aq})])^2}{K_{eq} [\text{Cl}^-(\text{s})]_{\text{sat}} + \varepsilon (1 + K_{eq} [\text{Cl}^-(\text{aq})])^2} \frac{\partial^2 [\text{Cl}^-(\text{aq})]}{\partial x^2} \quad (6.2.1)$$

$$[\text{Cl}^-(\text{s})] = \frac{K_{eq} [\text{Cl}^-(\text{aq})]}{1 + K_{eq} [\text{Cl}^-(\text{aq})]} [\text{Cl}^-(\text{s})]_{\text{sat}} \quad (6.2.2)$$

$$\text{initial condition:} \quad [\text{Cl}^-(\text{aq})] = [\text{Cl}^-(\text{aq})]_{\text{in}} \text{ at } t = 0 \quad (\text{initial concentration}) \quad (6.2.3)$$

$$\text{boundary conditions:} \quad [\text{Cl}^-(\text{aq})] = [\text{Cl}^-(\text{aq})]_0 \text{ at } x = 0 \quad (\text{concrete surface}) \quad (6.2.4a)$$

$$\partial [\text{Cl}^-(\text{aq})] / \partial x = 0 \text{ at } x = M \quad (\text{axis of symmetry}) \quad (6.2.4b)$$

The total chloride concentration $[Cl^-(total)]$ (in kg/m^3 concrete) is the sum of chlorides in solid and aqueous solution, i.e., $(\epsilon[Cl^-(aq)]+[Cl^-(s)])$. In the above equations, x is the distance from the concrete surface (m), t is the time (s), D_{e,Cl^-} denotes the intrinsic effective diffusivity of Cl^- in concrete (m^2/s), K_{eq} the equilibrium constant for Cl^- binding (m^3 of pore volume/kg), $[Cl^-(s)]_{sat}$ the saturation concentration of Cl^- in the solid phase (kg/m^3 concrete), and ϵ the concrete porosity (m^3 pore volume/ m^3 concrete). As observed from Eq. (6.2.2), the chloride binding capacity depends both on $[Cl^-(s)]_{sat}$ (content of sites which can bind chlorides) and K_{eq} (ratio of adsorption to desorption rate constants).

As observed from Eq. (6.2.1), chloride ingress is retarded as D_{e,Cl^-} decreases, $[Cl^-(s)]_{sat}$ increases, or K_{eq} increases. When an SCM is added in concrete, chloride binding capacity increases, as experimental results showed ([81], higher total chloride content in a thin layer near the external mortar surface). This may be attributed to higher CSH content, especially that with lower C/S ratio, which can bind Na^+ ions and, therefore, the accompanying Cl^- . On the other hand, the pore restructuring due to pozzolanic products may decrease intrinsic diffusivity as well. As observed by scanning electron micrograph [81], a fine network of pozzolanic product (CSH) has been created in the middle of a capillary pore acting as a trap for chlorides. Using atomic force microscopy [104], it was found that the internal surface of the SCM-cement pastes presents small spheroid bulges giving an additional roughness.

The picture is different when a non-interacting molecule diffuses in a concrete incorporating SCM, as observed from carbonation results [31,81]. The ratio of oxygen to chloride diffusion coefficients was found constant for portland pastes of high W/C ratio but can attain high values for fine-textured blended cement pastes which have not suffered drying/carbonation [105]. It has also been reported [106] that this ratio increases as W/C ratio decreases. Also, it was found [107] that in the presence of chlorides the diffusivity of dissolved oxygen into saturated concretes decreases over and above the decrease of oxygen solubility in solution. It has also been reported [108], that up to a fly ash level of 33% the intrinsic air permeability remains fairly constant and then is higher compared to the control. The apparent chloride diffusion coefficient was found to decrease by a factor of 7. Chloride binding capacity increases by a factor of 4 and then remains constant. It seems, therefore, that chloride binding capacity is the determining factor in improving resistance to chloride ingress.

6.2.2 Parameter estimation

In the case of “complete” hydration and pozzolanic action, and for typical composition of the cementing materials, the *total porosity of concrete* can be calculated from Eq. (3.2.17), (3.2.28), (3.2.35) or (3.2.43).

The *intrinsic effective diffusivity* of Cl⁻ in concrete (m²/s), can be estimated by the following semi-empirical equation [31,81, for NaCl; for CaCl₂ the numerator is 2x10⁻¹⁰]:

$$D_{e,Cl^-} = \frac{2.4 \cdot 10^{-10}}{\left(\frac{K + CS + \sum (kP_{ACT})}{d_c} + \frac{W}{d_w} \right)^2} (\epsilon_{eff})^{3.5} \quad (6.2.5)$$

P_{ACT} is the active content of each SCM added either as cement constituent or as concrete addition (kg/m³), having an efficiency factor k. This is given in the previous section 3, as S_{ACT}, F_{ACT}, P_{ACT}, or SL_{ACT}. In Eq. (6.2.5), k is the *efficiency factors regarding chloride penetration* for each SCM added either as cement constituent or as concrete addition (see Table 6.2.1 for experimental values). Parameter ε_{eff} is an *effective, for diffusion, porosity*, calculated as follows:

$$\epsilon_{eff} = W/d_w - 0.226 \cdot 10^{-3} \{K + CS + \sum (kP_{ACT})\} \quad (6.2.6)$$

If *sea attack* concerns, the *chloride concentration in the aqueous solution* at the concrete surface, [Cl⁻(aq)]₀ (kg/m³ pore solution), depends on the sea, e.g., Atlantic Ocean and Mediterranean Sea: 20 kg/m³, North Sea: 16 kg/m³, Baltic Sea: 4 kg/m³.

In the case of de-icing salts, the estimation of [Cl⁻(aq)]₀ involves uncertainties due to many unknown parameters (frequency and quantity of salt spreading, amount of available water from rain or melted snow for salt dissolution, etc.). As a matter of fact, high Cl⁻ concentrations of 100 kg/m³ are usual. As the salt spreading takes place only a few months per year and moreover due to washing by rain the chloride surface concentration decreases, an exposure

Table 6.2.1 Efficiency factors (k-values) regarding chloride penetration for various supplementary cementing materials [31,81]*.

	Cementitious/ pozzolanic materials	Chloride resistance
1	Portland clinker	1
2	Blast furnace slag	2.2
3	Silica fume	6
4	Pozzolana (natural)	1
5	Metakaolin	5
6	Siliceous fly ash	3
7	Calcareous fly ash	2.2
8	Burnt shale	2.2
9	Limestone	0.1
10	Various SCM for CEM II	2.2
11	Various SCM for CEM IV	3
12	Various SCM for CEM V	3

* All these SCM were ground prior to use up to a fineness of $400 \pm 20 \text{ m}^2/\text{kg}$ according to Blaine's test.

equivalent to a concentration of 20 kg/m^3 continuously all year round can be adopted as a first approximation. However, a more realistic approach based on statistical data should be sought.

Another important conclusion from parametric analyses on chloride penetration [102] should be mentioned here. Let us suppose that the exposure of the concrete surface to chlorides is not continuous but *periodic*, dividing the total lifetime into a number of intervals of length T , during one part, ρT , of which the surface is considered to be exposed to chloride ingress, while during the rest, $(1-\rho)T$, it is not. Pore saturation conditions, however, were not considered to be affected by the change in exposure conditions. Results showed that *the free chloride concentration* at any time and distance ($[\text{Cl}^-(\text{aq})]_\rho$) is *independent of total duration T* of the exposure-nonexposure cycle, increases linearly with the “*exposure ratio*”, ρ , and it can be calculated by multiplying that of the continuous exposure ($[\text{Cl}^-(\text{aq})]_{\rho=1}$) by the ρ , i.e.:

$$[\text{Cl}^-(\text{aq})]_\rho = \rho [\text{Cl}^-(\text{aq})]_{\rho=1} \quad (6.2.7)$$

The above conclusion is very important and it can be applied in the case of de-icing salts. In other words, if the exposure ratio is $\rho=0.2$ (1/5 of the year) for concrete subjected to contact with water containing chlorides originating from de-icing salts of a concentration of 100 kg/m^3 , the free- Cl^- concentration will be the 0.2 of that of the continuous exposure.

Parameters $[\text{Cl}^-(\text{s})]_{\text{sat}}$ and K_{eq} can be determined from chloride binding isotherms. An experimental approach described in **Appendix A** was followed. The *equilibrium constant for Cl⁻ binding* was found fairly constant for all mixtures ($K_{\text{eq}} = 0.1 \text{ m}^3$ of pore volume/kg Cl^-). For *saturation concentration of Cl⁻ in the solid phase*, the following empirical expression may be used [31,81,103]:

$$[\text{Cl}^-(\text{s})]_{\text{sat}} = 8.8 \cdot 10^{-3} \{K + \text{CS} + \sum(kP_{\text{ACT}})\} \quad (6.2.8)$$

$$K_{\text{eq}} = 0.1 \text{ m}^3 \text{ pore volume/kg } \text{Cl}^- \quad (6.2.9)$$

6.2.3 Chloride threshold for reinforcement corrosion

A way of threshold expression is by measurement the *total chloride ion content in concrete required for the onset of reinforcement corrosion*. This approach embodies inaccuracies because only the free chlorides present in pore solution cause corrosion.

However, it is very often reported that **if the total chloride content is more than 0.4% bw of cement, the steel is activated and corrosion may occur**. It has been demonstrated [109] that the chloride threshold for uncracked SRPC (sulphate-resistant portland cement) concrete with low W/C ratio (0.3-0.5) is in the range of 1-1.3% total chloride bw of binder, for SRPC concrete with 5% SF in binder is 0.8-1.0%, and with 10-20% fly ash in the binder is about 0.7%. Moreover, it is generally accepted [10] the following description of the corrosion risk:

- less than 0.4% chloride by mass of cement: low risk
- 0.4 – 1.0% chloride by mass of cement: medium risk
- greater than 1.0% chloride by mass of cement: high risk

In the case of use of additions the binder quantity has rather to be taken into account. Multiplying by the cementitious materials' content in concrete, a lower and an upper limit could be defined:

$$[\text{Cl}^-(\text{total})]_{\text{cr},\text{min}} = 0.004 \{K+\text{CS} + \sum(\text{P}_{\text{ACT}})\} \text{ kg total chlorides/ m}^3 \text{ concrete} \quad (6.2.10)$$

$$[\text{Cl}^-(\text{total})]_{\text{cr},\text{max}} = 0.012 \{K+\text{CS} + \sum(\text{P}_{\text{ACT}})\} \text{ kg total chlorides/ m}^3 \text{ concrete} \quad (6.2.11)$$

However, for final design a mean value of critical total chloride content for corrosion of reinforcement is proposed:

$$[\text{Cl}^-(\text{total})]_{\text{cr}} = 0.008 \{K+\text{CS} + \sum(\text{P}_{\text{ACT}})\} \text{ kg total chlorides/ m}^3 \text{ concrete} \quad (6.2.12)$$

6.2.4 Model solution

Eq. (6.2.1) can be solved only *numerically*, e.g., using a finite difference or element method, for the given initial and boundary conditions, Eqs. (6.2.3)-(6.2.4). The solution gives the free- Cl^- concentration, $[\text{Cl}^-(\text{aq})]$, for various distances x in the concrete mass and at various ages, t , and by applying Eq. (6.2.2), the bound- Cl^- concentration, $[\text{Cl}^-(\text{s})]$ is calculated. The total chloride concentration $[\text{Cl}^-(\text{total})]$ (in kg/m^3 concrete) is the sum of chlorides in solid and aqueous solution, i.e., $(\varepsilon[\text{Cl}^-(\text{aq})]+[\text{Cl}^-(\text{s})])$. The solution allows estimation of the time (**critical time for chloride-induced corrosion, $t_{\text{cr,chlor}}$**) required for the total chloride concentration surrounding the reinforcement (located at a distance c from surface- *cover*) to increase over the threshold for depassivation, $[\text{Cl}^-(\text{total})]_{\text{cr}}$. We can state the following:

✚ The service lifetime of a structure, regarding chloride penetration, is at least $t_{\text{cr,chlor}}$.

Afterwards, the propagation of corrosion process takes place at a rate that depends strongly on the availability of both oxygen and water. The following sections offer a qualitative prediction of the propagation period. Only as a first approximation, the corrosion rates presented in the carbonation section may be used.

6.3 Corrosion of the reinforcement in chloride-rich concrete

6.3.1 Estimation of the corrosion propagation period

The anodic reaction is of particular interest in the case of chloride-rich concrete, i.e., when the Cl^- concentration has exceeded the critical value for corrosion at the reinforcement area [1,7,10, 110]. The anodic process consists of the following steps, see also Fig. 6.3.1:



There follows a consequent recycling of the liberated chloride ions. Although corrosion product is being produced at this particular point of bar (pitting corrosion) so too H^+ and Cl^- . The increased acidity of the anodic area helps to prevent precipitation of corrosion product and it encourages further oxidation of the iron bar.

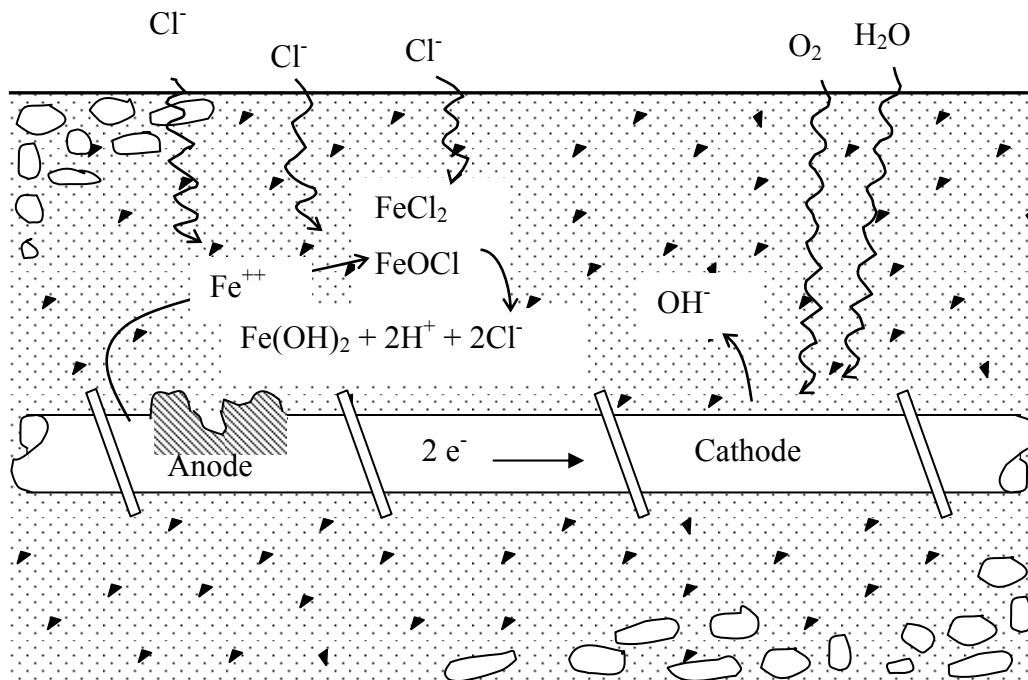


Figure 6.3.1 Mechanisms and results of pitting corrosion in a chloride-rich environment.

However, the rate of corrosion is influenced by the availability of O_2 and H_2O at the cathode, that is not straightforward because even low rates of O_2 supply may lead to a severe pitting corrosion. This effect occurs because the anodic sites may be localized but the corresponding cathodic sites may be spread out over a wide area. The cumulative effect of even low rates of O_2 supply to large cathodes may be significant. As the corrosion product is discouraged from precipitation, and due to the existence of highly active and localized anodic sites, a severe pitting corrosion may occur without an earlier warning through visible signs at the surrounding concrete. This can lead to rapid loss of cross-section and critically reduce the load bearing capacity of the reinforced concrete member. When cracks do develop, the corrosion product will then be deposited along the crack. By the time rust staining becomes apparent at the surface, the extent of reinforcement deterioration may be structurally significant.

The possible mechanism of chloride ion interaction with the reinforcement and passive layer has not been fully resolved. Moreover, the estimation of propagation period and the definition of the end of the service life due to chloride-induced corrosion are also contain a lot of uncertainties [84-86, 111-113]. Therefore, as in the case of carbonation, *the time $t_{cr, chlor}$ required for Cl^- to exceed the critical value at the concrete cover c can be considered in good approximation as a narrow lower bound to the service life of reinforced concrete.*

6.3.2 Relationship with EN 206

The passivity of the reinforcement is depended on the stability of the passive film formed on it when the steel is found in the alkaline environment of the fresh concrete. This passive film is rendered ineffective when the Cl^- level in the surrounding concrete exceeds a critical value. The internal sources of Cl^- are currently limited to tolerable levels by specification. For example, the European Standard EN 206-1 [12] limits the chloride content in a range of 0.1-0.4% of cement by mass in the case of reinforced concrete. Especially, the chloride content of a concrete, expressed as the percentage of chloride ions by mass of cement, shall not exceed the value for the selected class given in Table 6.3.1. The strictest limitations apply to prestressed concrete. Aggregate standards also limit the chloride content of aggregate for use

in concrete. The use of seawater, chloride-bearing aggregates or admixtures (e.g., CaCl_2) is thus strictly controlled.

Table 6.3.1 Chloride content classes and maximum chloride content of concrete according to EN 206-1.

Concrete use	Chloride content class	Maximum Cl^- content by mass of cement
Not containing steel reinforcement or other embedded metal with the exception of corrosion-resisting lifting devices	Cl 1,0	1.0 %
Containing steel reinforcement or other embedded metal	Cl 0,20	0.20 %
	Cl 0,40	0.40 %
Containing prestressing steel reinforcement	Cl 0,10	0.10 %
	Cl 0,20	0.20 %

Chloride penetration is a process which takes place in totally or partly water-filled pores. This is the main reason that as a process is much slower than carbonation, where CO_2 molecule may penetrate faster via air-filled pores. The moisture availability of the environment and the origin of Cl^- were taken into account in the definition of the *exposure classes in EN 206*. As in the case of carbonation and corrosion processes, chloride penetration and corrosion require water. In this case, chloride penetration and corrosion are much faster at higher water contents of concrete pores, and consequently at higher moisture contents of the ambient environment [1,10]. This was taken into account in the definition of the exposure classes according to EN 206, and a correlation with the mean relative humidity of the ambient environment is presented in Table 6.3.2 [this work; 1,10]. An estimation of the corrosion risk for various relative humidity regions is also presented [this work, 1].

In order to investigate if the EN 206 recommendations for limiting composition values would ensure a service life of 50 years, the above mathematical model was used, and the results are presented in Table 6.3.3. Typical cement types were examined, CEM I 42,5N and CEM II/B-M 32,5N, for concrete production, using common crushed aggregates of maximum size of 31.5 mm. An air content of 3% was assumed.

Table 6.3.2 Exposure classes according to EN 206 for possible corrosion induced by chlorides, correlation with measurable relative humidity (RH) and estimation of chloride penetration and corrosion risks.*

Class	Description of the environment	Informative examples	RH (%)	Cl ⁻ risk	Corr. risk
No risk of corrosion or attack					
X0	For concrete with reinforcement or embedded metal: Very dry	Concrete inside buildings with very low air humidity	<45	0	0
Corrosion induced by chlorides from sea water					
Where concrete containing reinforcement or other embedded metal is subjected to contact with chlorides from sea water or air carrying salt originating from sea water, the exposure shall be classified as follows:					
XS1	Exposed to airborne salt but not in direct contact with sea water	Structures near to or on the coast	< 80	1	2
XS2	Permanently submerged	Parts of marine structure	> 98	3	1
XS3	Tidal, splash and spray zones	Parts of marine structure	> 80	3	3
Corrosion induced by chlorides other than from sea water					
Where concrete containing reinforcement or other embedded metal is subjected to contact with water containing chlorides including de-icing salts, from sources other than from sea water, the exposure shall be classified as:					
XD1	Moderate humidity	Concrete surfaces exposed to airborne chlorides	< 80	1	2
XD2	Wet, rarely dry	Swimming pools, concrete exposed to industrial waters containing chlorides	> 98	3	1
XD3	Cyclic wet and dry	Parts of bridges exposed to spray containing chlorides, pavements, car park slabs	> 80	3	3

* Risk: 0 = not significant, 1 = slight, 2 = medium, 3 = high

In the case of concrete containing reinforcement and subjected to contact with **chlorides from sea water**, for all exposure classes: **XS1**: exposed to airborne salt but not in direct contact with sea water (structures near to or on the coast), **XS2**: permanently submerged (parts of marine structure), **XS3**: tidal, splash and spray zones (parts of marine structure), the recommendations of EN 206 ensure a service life greater than 50 years (even 100 years); for

an adequate cover, see Table 6.3.3. We suppose a non-protected concrete surface, exposed to Atlantic Ocean environment (Cl^- concentration: 20 kg/m^3). It has to be emphasized that on the contrary to the carbonation results, cement types that contain supplementary cementing materials (SCM: silica fume, fly ash, etc.) exhibit significantly longer initiation period than the pure portland cement.

Table 6.3.3 Estimated lower bound of concrete service life for various cement types and exposure classes, in the case of chloride-induced corrosion of reinforcement.

COMPOSITIONAL AND DESIGN CHARACTER.	XS1	XS2	XS3	XD1	XD2	XD3
Cement type CEM I 42.5N						
Maximum ratio W/C	0.50	0.45	0.45	0.55	0.55	0.45
Minimum content C (kg/m^3)	300	320	340	300	300	320
Minimum strength class	C30/37	C35/45	C35/45	C30/37	C30/37	C35/45
$t_{\text{cr,chlor}}$ (years) for $c = 30 \text{ mm}$	63	25	32	43	8	32
$t_{\text{cr,chlor}}$ (years) for $c = 35 \text{ mm}$	80	35	46	57	12	43
$t_{\text{cr,chlor}}$ (years) for $c = 40 \text{ mm}$	100	48	58	72	16	53
$t_{\text{cr,chlor}}$ (years) for $c = 45 \text{ mm}$	>100	58	70	90	20	64
$t_{\text{cr,chlor}}$ (years) for $c = 50 \text{ mm}$	>100	69	81	>100	24	77
Cement type CEM II/B-M(W-P-LL) 32.5N						
Maximum ratio W/C	0.50	0.45	0.45	0.55	0.55	0.45
Minimum content C (kg/m^3)	300	320	340	300	300	320
Minimum strength class	C25/30	C30/37	C30/37	C25/30	C25/30	C30/37
$t_{\text{cr,chlor}}$ (years) for $c = 30 \text{ mm}$	70	38	35	54	15	46
$t_{\text{cr,chlor}}$ (years) for $c = 35 \text{ mm}$	100	50	48	78	20	59
$t_{\text{cr,chlor}}$ (years) for $c = 40 \text{ mm}$	>100	67	60	>100	28	78
$t_{\text{cr,chlor}}$ (years) for $c = 45 \text{ mm}$	>100	84	75	>100	37	>100
$t_{\text{cr,chlor}}$ (years) for $c = 50 \text{ mm}$	>100	100	95	>100	46	>100

W/C: water to cement ratio by weight, C: cement content in concrete (kg/m^3), c : concrete cover to reinforcement (mm), $t_{\text{cr,chlor}}$: initiation period for chloride-induced corrosion of reinforcement.

In the case of concrete with reinforcement and subjected to contact with **water containing chlorides including de-icing salts**, from sources other than from sea water, for all exposure classes: **XD1**: moderate humidity (concrete surfaces exposed to airborne chlorides), **XD2**: wet, rarely dry (swimming pools, concrete exposed to industrial waters containing chlorides), **XD3**: cyclic wet and dry (parts of bridges exposed to spray containing chlorides, pavements, car park slabs), the recommendations of EN 206 ensure a service life greater than 50 years (in some cases even 100 years); for an adequate cover, see Table 6.3.3. Especially for XD2, in spite of the low initiation period, the total life is much longer due to prolonged propagation period; however, a denser design may be required. We suppose a non-protected concrete surface, exposed to a Cl^- concentration of 100 kg/m^3 , lasting for 1/5 of the year. In this case also blended cements with SCM, or when an SCM is added separately to the concrete mixture, the estimated initiation period is greater than in the case of pure portland cement use.

6.4 Protection measures

6.4.1 Protection against corrosion

Although many recommendations for concrete cover and quality aimed at extending the initiation period in corrosion ($t_{\text{cr, chlor}}$) as far as possible, there are circumstances in which it is impossible to prevent corrosion being initiated. Much research has therefore been carried out to determine the factors that control *the corrosion rate at the propagation period*. Some of the most important conclusions are summarized in the following [44]:

1. *The spacing and relative size of the anode and cathode in the corrosion cell.* Relatively porous areas of a concrete member will allow rapid penetration of chlorides, depassivating a small area of steel to form the anode. The remainder reinforcement forms a large cathode area, resulting in a concentration of the corrosion current, and hence a high corrosion rate, at the anode.
2. *The availability of oxygen and moisture, particularly to sustain the cathodic reaction.* If the supply of either is reduced, then the corrosion rate is reduced. Hence little corrosion occurs in completely dry concrete, and little also in permanently saturated concrete, through which O_2 diffusion is difficult.

3. *The electrical resistivity of the electrolyte of the corrosion cell, i.e., the concrete.* By increasing moisture content, chloride content and porosity, the resistivity of concrete is reduced, and hence the corrosion rate is increased. The use of SCM either as cement constituents or as concrete additions can also reduce dramatically the chloride penetration and further the corrosion rate.

In the circumstances when protection against corrosion cannot guaranteed by selection of the materials and proportions of the concrete, depth of cover and attention to sound construction practice, one or more of the following **extra protective measures** may then be taken [1,44, 114]:

- The addition of a *corrosion inhibiting admixture*, such as calcium nitrite, to the fresh concrete.
- The use of *corrosion-resistant stainless steel* reinforcing bars, or *epoxy-coated* conventional bars.
- *Cathodic protection of the reinforcement*, i.e., applying a voltage from an external source sufficient to ensure that all of the steel remains permanently cathodic.
- Applying a *protective coating or an impregnation technique to the concrete*, to reduce chloride, moisture and/or oxygen ingress.

6.4.2 Protection by using waterproof sealants

Let us suppose the case of exposure in an *aggressive environment* (presence of seawater or de-icing salts). Let us suppose also that in some parts of the structure, a *failure* in the designed cover occurred or a cover less than the recommended one was selected, due to technical or economical reasons. If the same service life is required, then the concrete surface should be covered by a protective coating (i.e., an *asphalt membrane*) to maintain the same lifetime. However, this coating can be considered as waterproof only for some years, say X . Then, the chlorides can easily attack the concrete through coating holes for some years, say Y . Then, a repair takes place which will protect the concrete for X years, and the cycle again starts. Let us suppose that the number of repairs is n within the designed service lifetime, Z , (a small number of 2-5 should be expected). Thus:

$$Z = n (X + Y) \quad (6.4.1)$$

$$\rho = Y / (X + Y) \quad (6.4.2)$$

where, ρ is the *exposure ratio* (see on 6.2.2 section). As mentioned, the free chloride concentration at any time and distance is independent of the number of repairs, n , and it can be calculated by multiplying that of the continuous exposure by the exposure ratio, ρ . Thus, the free chloride concentration at the designed service lifetime, Z , at any distance from the concrete surface, is given by:

$$\varepsilon [\text{Cl}^-(\text{aq})]_{\rho,Z} = \rho \varepsilon [\text{Cl}^-(\text{aq})]_{\rho=1,Z} \quad (\text{denoted as } \mu) \quad (6.4.3)$$

In order to ensure reinforcing bar protection at a given cover c , the following requirement should be fulfilled:

$$\mu + \frac{K_{eq} \mu}{\varepsilon + K_{eq} \mu} [\text{Cl}^-(\text{s})]_{\text{sat}} \leq [\text{Cl}^-(\text{total})]_{cr} \quad (6.4.4)$$

Having calculated the free chloride concentration for the case of continuous exposure ($\rho=1$) at the design service lifetime of Z years, the dependence of concrete cover on exposure degree can be estimated, see an example in [31]: As the problem is independent of the number of repairs, any n can be selected, say $n=5$, thus in a design service lifetime of 100 years, the coating shall be repaired every 20 years. Let us suppose that the mean concrete cover in a part of the structure is 30 mm. According to [31] example, a maximum exposure degree of $\rho=0.3$ is calculated. This means that the coating shall be completely waterproof for at least $(1-0.3) \cdot 20 = 14$ years within the 20-year period. If $n=2$ is selected, then the coating shall be waterproof for 35 years in a 50-year period.

